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Abstract
Compositions located in the metastable miscibility gap of BiZn immiscible alloy was investigated under a high static magnetic field (HSMF). BiZn immiscible alloys with uniformly distribution of solid particles in the matrix were obtained under HSMF with 29 T. The results show that the solid Bi particles were uniformly distributed in the matrix because of complete suppression of Stokes sedimentation under the HSMF with 29 T. Segregation in the alloys solidified under 0 T, 1 T and 6 T was mainly owning to Stokes sedimentation, but that solidified under 17.4T and 29 T was dominated by nucleation, growth and Marangoni migration processes of liquid Bi droplets. The segregation mechanism under the effects of HSMF was discussed.

Key words: High static magnetic field, Immiscible alloys, Segregation, Solidification

Introduction

Immiscible alloys, which are known as monotectic alloys, have been investigated for decades because of the excellent conductivity [1], wear resistance [2] and fine optics performance. However, the solidified structure with segregation will arise at the normal gravity condition mainly because of Stokes sedimentation induced by the action of large density difference between the two elements in binary alloys and Marangoni convection caused by thermo-gradient. So it is necessary to design new methods to manufacture immiscible alloys with fine particles dispersing in matrix through suppressing or avoiding Stokes sedimentation and Marangoni convection.

Recently years, as a non-contact energy, high static magnetic fields (HSMFs) have been successfully applied during the solidification process of immiscible alloys. Based on the previous research of J. Wang [3], the aims of this paper are trying to make a wholly investigation on the effects of magnetic field on the migration of liquid and solid droplets and microstructures of Zn-Bi alloys. And it also discusses the factors that led to the segregation at different magnetic flux densities in a proper way. In the meantime, this paper reports that Bi-0.44Zn and Bi-0.98Zn (mole fraction) immiscible alloys with an ideal microstructure was obtained under 29 T HSMF for the first time. The effects of HSMF on the Stokes sedimentation and Marangoni migration are also discussed.

Experimental detail

Bi-0.44Zn and Bi-0.98Zn alloys were prepared by Zn particles (purity of 5 N) and Bi particles (purity of 5 N). The mixed particles were placed into a quartz tube with an inner diameter of 10 mm and a length of 150 mm and then heated to 975 K (above T_c) and held for 30 min to get a columnar ingot with 10mm in diameter by using a vacuum electro-magnetic induction heating furnace under the protection of highly pure Ar gas. Then, all samples were remelted at 975 K and held for 1 h. When the holding time is over, the melts were in-situ quenched into water (cooling rate was about 20 K/s) without or with a vertical HSMF respectively.

The solidified samples were sectioned along the direction parallel and perpendicular to the HSMF and then polished mechanically. The microstructures and morphologies were characterized by using the function of Back Scattered Electron Imaging (BSE) of scanning electron microscopy (SEM, VEGA3 SBH-Easyprobe).

Results and discussion

As mentioned in the first part, Stokes sedimentation plays an important role in gravitational direction. For Bi-Zn immiscible alloy system, the immiscible gap can be divided into two regions. One is metastable against concentration fluctuations (at constant temperature) and locates between binodal line and spinodal line. The other is instable against even the smallest concentration fluctuation and locates below the spinodal line [4]. This means that phase decomposition of the mixed liquid (L) into Zn-rich liquid (L1) and Bi-rich liquid (L2) occurs below the binodal line by nucleation and growth, thus there is an energy barrier to overcome. If a mixed liquid is cooled below the spinodal line any concentration fluctuation will be amplified, and there is no energy barrier to decomposition. The compositions that we chose belong to metastable miscibility gap which are located in the gap between binodal line and spinodal line. In other words, during the whole process of solidification, Bi-0.44Zn and Bi-0.98Zn alloys will not experience the instable region. This indicates that these two alloys may be easily to be manufactured by in-situ quenching method in HSMF. As we know, severely longitudinal segregation is formed because of the Stokes sedimentation under a normal gravity condition.

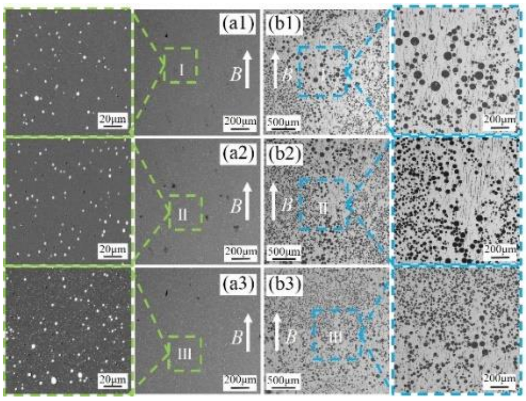

Fig. 1: BSE pictures of longitudinal microstructures of Bi-0.98Zn and Bi-0.44Zn under 29 T. a1-a3) are microstructures at the top, middle and bottom of Bi-0.98Zn alloy. b1-b3) are microstructures at the top, middle and bottom of Bi-0.44Zn alloy respectively

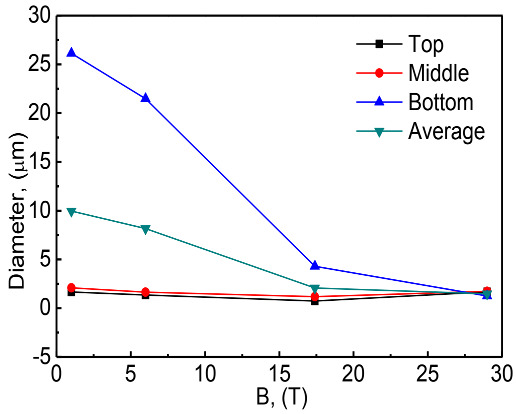

Fig. 2: The relationship between the diameter of Bi-rich droplets and magnetic flux density.

Bi-0.44Zn and Bi-0.98Zn alloys with the composition locating in metastable miscibility gap were studied under 29 T. The longitudinal microstructures along central axis of ingot are shown in Fig. 1. From Fig. 1, we find that the dimensions of Bi-rich droplets in Bi-0.98Zn alloy and Zn-rich droplets (back color in Fig. 1b1-Fig. 1b3) in Bi-0.44Zn alloy are uniformly distributed in top, middle and bottom parts. Thus, the Stokes sedimentation was almost completely suppressed by HSMF with 29 T.

The dimensions of Bi-rich droplets were collected systematically and their relationship between magnetic flux density is shown as Fig. 2. The diameters of Bi-rich particles were significantly decreased as the increase of magnetic flux density gradually. By superimposing HSMF with 1 T and 6 T, the diameters of Bi-rich droplets at the bottom part were bigger than 10 μm and reached to 27 μm. But when magnetic flux density was increased up to 17.4 T and 29 T, the droplets throughout the ingots were smaller than 10 μm. Furthermore, the maximum diameters (d_m) of Bi-rich droplets at the bottom part of Bi-0.98Zn alloys solidified under 1 T, 6 T, 17.4 T and 29 T were 253.23 μm (d_{1m}), 95.83 μm (d_{2m}), 10.91 μm (d_{3m}) and 2.59 μm (d_{4m}) respectively. As the calculation shown in the previous study [5, 6], droplets with size of order of 1 μm are big enough to produce a sufficient surface tension difference between the hot and cool parts for a migration, which is called Marangoni migration. The Stokes sedimentation takes place when the diameter of droplets is bigger than 10 μm.

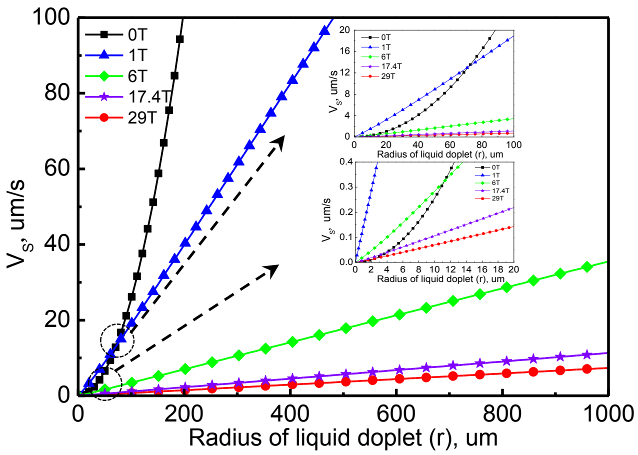

Fig. 3: Velocity of Stokes migration versus droplet radius for Bi-0.98Zn alloy in metastable miscibility gap.

Stokes sedimentation is affected by the difference of density between Zn element and Bi element under gravitational condition. It determines the segregation along the longitudinal direction when the sample was solidified at a normal gravity condition. Velocity of Stokes sedimentation without magnetic field can be described by the Hadamard-Rybczynski relation [7]:

$$V_S = \frac{2gr^2(\rho_2 - \rho_1)(\eta_1 + \eta_2)}{3\eta_1(2\eta_1 + 3\eta_2)} \tag{1}$$

where g is gravity constant, ρ_1 and ρ_2 are the densities of L1 and L2 respectively, η_1 and η_2 represent the viscosities of L1 and L2 respectively, r represents the radius of liquid droplet. Based on eq. (1), it can be seen that the V_s will be significantly decreased as the decrease of r. The radius of liquid droplet can be decreased through the suppression effects of HSMF on the droplets collision [8], nucleation and growth processes. The physical parameters used in this paper are given in Table 1. In addition, HSMF affects the Hartman number that is used to calculate the viscosity of the matrix ($\eta_{eff}=\eta_1\mathrm{Ha}/3=2B\cdot r\cdot(\sigma\eta_1)^{0.5}/3$) [8, 3]. If we assume Ha > 1 [8], the velocity of Stokes migration can be calculated by replacing η_1 as η_{eff} in eq. (1). Fig. 3 shows the relationship of velocity of Stokes migration versus droplet radius for Bi-0.98Zn alloy in metastable miscibility gap. In Fig. 3, it is clearly shown that four intersections appear between the lines with and without HSMF.

However, we found that Marangoni migration of droplets still remained in the region closing to crucible wall in both Bi-0.98Zn and Bi-0.44Zn ingots. The velocity of Marangoni migration without magnetic field [9] can be expressed as:

$$V_M = -\frac{2\kappa_1 r}{(2\kappa_1 + \kappa_2)(2\eta_1 + 3\eta_2)}\frac{d\sigma}{dT}\nabla T \tag{2}$$

where κ_1 and κ_2 are the thermal conductivities of L1 and L2 respectively, $d\sigma/dT$ is the temperature coefficient of interfacial tension, ∇T is temperature gradient. Just as discussed above, the viscosity of matrix was affected by HSMF. If we define V_m* as the velocity of Marangoni migration under HSMF. Then, η_1 should be replaced by an effective viscosity (η_{eff}) [3].

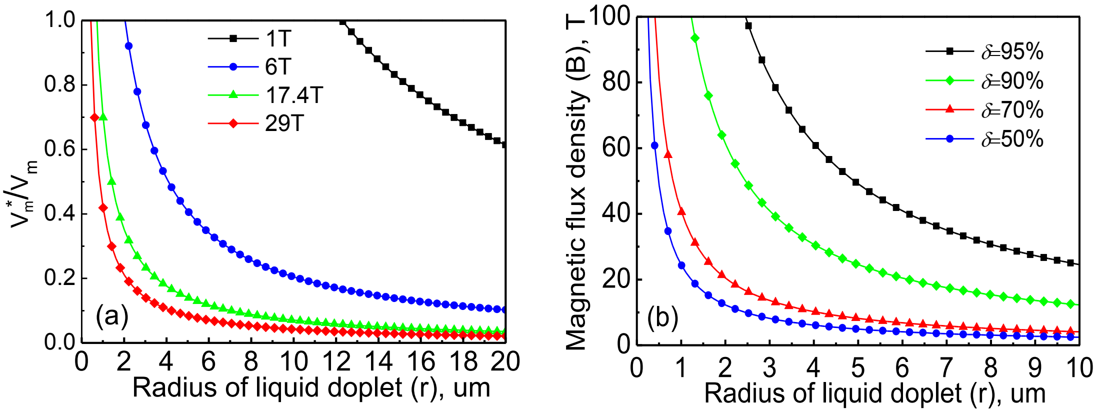

Fig. 4: (a) The radius of droplet versus the percentage ratio of the velocity of Marangoni migration with and without HSMF, (b) The relationship between the magnetic flux density and the radius of droplet

In order to easily illustrate the suppression efficiency, we defined it as a percentage ratio of the velocity of Marangoni migration with and without HSMF (V_m*/ V_m). From Fig. 4a, it can be seen that the Marangoni migration was gradually suppressed by increasing HSMF from 1 T to 29 T at the condition of same radius. Based on our calculated results, the Marangoni migration was suppressed by 70% for Bi-0.98Zn alloy and by 95% for Bi-0.44Zn alloy at 29 T. Therefore, the microstructure of Bi-0.98Zn alloy was controlled by a cooperative action of Marangoni migration, nucleation and growth processes at 29 T.

Conclusions

In-situ quenching solidification method was used in solidifying BiZn immiscible alloy under the condition of high static magnetic fields. Stokes sedimentation was the main reason that led to the longitudinal segregation at 0 T, 1 T and 6 T. Marangoni migration was the main reason that led to the slightly longitudinal segregation at 17.4 T. Both Stokes sedimentation and Marangoni migration were almost completely suppressed by HSMF with 29 T. Bi-0.98Zn and Bi-0.44Zn alloys with a uniform distribution of solid particles in the matrix were obtained at 29 T. The distribution of solid particles in the alloys solidified at 29 T was mainly dependent on the effects of HSMF on the stages of nucleation, growth and Marangoni migration.

Acknowledge

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